

REMARKS

Reconsideration is respectfully requested. Claims 1-50 were present in the application. Claims 1, 6, 7, 11, 12, 14, 17, 18 and 19 are amended herein. Claims 8, 9, 10, 15 and 16 are canceled. Non-elected claims 2-5 and 20-50 are canceled. New claims 51-67 are added

Election was made of group I. The non-elected claims are canceled herein to further prosecution with reservation of the right to file divisional applications thereto.

Claims 8-19 are objected to as being multiple dependent claims dependent on other multiple dependent claims. Amendments herein are made to claims 11-14 and 17-19 to address this point. New claims 51-67 are added to retain some of the dependencies of claims 11-14 and 17-19 prior to amendment, but in single dependent form.

Claims 1, 6 and 7 are rejected under 35 U.S.C. §112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Applicant has amended the claims to remove the word 'type' and provide an alternate expression of 'nitrogen in solid solution'.

Claims 1, 6 and 7 are rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Miura et al "Composition

Dependence of Microstructure of Mechanically Alloyed Powders and Their Compacts of High Nitrogen Cr-Mn Steels" in view of Flinn et al (US5980486).

Applicants respectfully traverse.

It is noted that nitrogen in austenite steels strikingly enhances their ultimate Tensile strength (UTS) and yield strength (YS) with increase in the concentration without sacrificing toughness, up to about 0.4 mass % nitrogen as indicated in FIG. 1 of the attached reference, M.O. Speidel, Properties of High Nitrogen Steels, Proc. 2<sup>nd</sup> HNS, Aachen, 1990, pp. 128-131 (hereafter referred to as SPEIDEL REFERENCE).

However, when the nitrogen concentration in austenite steels exceeds approximately 0.4 to 0.5 mass %, their toughness steeply decreases, i.e., effect of nitrogen in austenite steels containing 0.5 mass % or more of nitrogen clearly differs with that seen in austenite steels containing up to about 0.4 mass % of nitrogen, as shown in FIG. 1 of the SPEIDEL REFERENCE.

On the other hand, even in such high nitrogen containing austenite steels when they contain about 0.30 to 1.0 mass % carbon (i.e., when carbon/nitrogen mass ration is favorably, near unity) as seen in the present claims, i.e. claims 12 and 14 as amended, short range ordering (SRO) leading to homogenization of distribution of alloying elements in the austenite phase is markedly promoted with increase in the carbon concentration through increase in the concentration of free electrons

providing more metallic character of interatomic bonds, so that in such austenite steels with both interstitial elements, nitrogen and carbon, not only the strength such as ultimate tensile strength (HTS) and yield strength (YS) but also the toughness is highly enhanced.

The present claimed invention is characterized in that said combination of nitrogen and carbon contained in austenite steel materials, which have not been manufactured by known techniques, also in their nitrogen concentration levels is as high as 0.50 mass % or more as mentioned above.

In view of the fact that the carbon concentration level in the austenite described in the Flinn et al patent, the Wilson patent (US4999052), and the Rhodes et al patent (US5841046) is as low as 0.01 to 0.08 mass %, 0.01 to 0.03 mass % and 0.03 to 0.08 mass % respectively, said effect due to combination of nitrogen and carbon cannot be expected to be produced in such austenite steels.

So far, no reports exist that describe the addition of carbon to the mechanically alloyed powder of nitrogen-rich austenite steel, followed by the consolidation process, to prevent decrease in the toughness of the consolidated austenite steel bulk material.

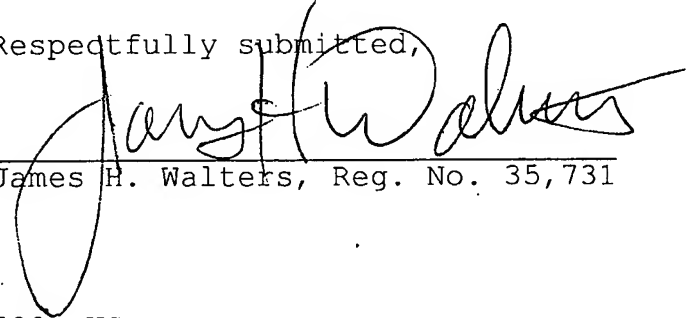
In view of the above, it is respectfully submitted Miura et al "Composition Dependence of Microstructure of Mechanically Alloyed Powders and Their Compacts of High Nitrogen Cr-Mn Steels"

in view of Flinn et al (US5980486) does not teach or suggest the claims.

In light of the above noted amendments and remarks, this application is believed in condition for allowance and notice thereof is respectfully solicited. The Examiner is asked to contact applicant's attorney at 503-224-0115 if there are any questions.

It is believed that no further fees are due with this filing or that the required fees are being submitted herewith. However, if additional fees are required to keep the application pending, please charge deposit account 503036. If fee refund is owed, please refund to deposit account 503036.

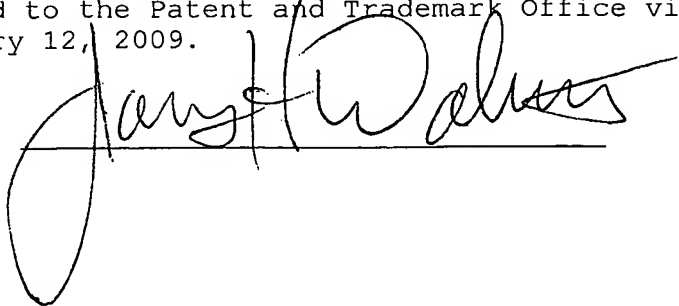
Respectfully submitted,

  
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# Properties of High Nitrogen Steels

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## Abstract

This paper highlights some of the most useful properties of high nitrogen austenitic and ferritic high nitrogen steels. Such properties include: strength, creep resistance, fracture toughness, stress corrosion resistance, magnetic properties and others.

It is shown that certain high nitrogen steels offer unique advantages by combining a number of outstanding values of the above mentioned properties. Naturally, there are also limitations and these are also mentioned.

It is indicated how the properties achievable with high nitrogen contents can give rise to new and useful applications.

## Introduction

For the purpose of the present paper, steels will be considered "high nitrogen" if, with a ferritic matrix they exceed 0.08 weight-percent nitrogen or if, with an austenitic matrix they exceed 0.4 weight-percent nitrogen. Such steels may have outstanding properties such as strength, toughness, creep rupture strength, stress corrosion resistance or wear resistance. What makes them particularly attractive, however, is the combination of such outstanding properties. In recent years, intensive development of high nitrogen steels has resulted in improved properties and new prospective applications.

The present paper highlights some of those useful properties of high nitrogen steels which will be presented in depth in several other contributions to the HNS 90-conference.

## Yield Strength, Fracture Toughness

An increase in yield strength has long been the major reason for the alloying of nitrogen to solution annealed austenitic stainless steels. Typical data are shown in the upper part of Fig. 1. With proper grain size control, yield strengths of 1000 MPa can now be reached and exceeded. It is remarkable that such a strong increase of strength is accompanied by an only moderate loss of fracture toughness, as shown in the lower part of Fig. 1. Up to about 0.8 weight-percent nitrogen, the fracture toughness properties of the solution annealed austenitic steels are exceedingly high when measured at ambient temperature. However, at cryogenic temperatures, a ductile-to-brittle transition is observed resulting in cleavage cracking of the face centered cubic crystals. This limits the applications of high nitrogen steels for cryogenic service.

The steep increase in strength at constant fracture toughness which is illustrated in Fig. 1 is quite unusual in metallurgical alloy developments, since most often an increase in strength is coupled with a loss of fracture toughness. This effect of solid solution hardening due to nitrogen atoms in face centered cubic materials is now being studied with entirely different base compositions, but the restricted solubility for nitrogen in most metals and alloys restricts the choice. Nevertheless, the principle should be applicable to other alloy systems.

## Ultrahigh Strength Nonmagnetic Stainless Steels

One of the most remarkable developments concerning high nitrogen steels is the attainment of higher and higher yield strength levels by judicious combination of all four basic hardening mechanisms: Solid solution hardening, grain boundary hardening, work hardening, and precipitation hardening (by nitrogen atoms precipitating at stacking faults akin to a "Suzuki" effect, not resulting in particles). As indicated in Fig. 2, a yield strength of 3000 MPa has recently been obtained - and this may be further optimized. It is important to notice that Fig. 2 characterizes only fully stable austenites which do not form martensite during plastic deformation. Naturally, this exceptionally high strength in a stable, nonmagnetic, austenitic stainless steel can be obtained so far only in components with thin cross sections, such as wire, band and sheet. Compared to the first use of austenitic stainless steel, the yield strength is now ten times higher. Since 3000 MPa yield strength is still far from the theoretical limit, further alloy development has ample scope for even higher strength. Many obvious applications can be considered since this high strength is coupled with other useful properties, for example nonmagnetic and stainless behavior.

### Strength and Toughness

A good quality index for the mechanical properties of steels is the product of yield strength times fracture toughness as indicated in Fig. 3. Note that modern steel development has resulted in a doubling of this quality index every decade since 1960. High nitrogen austenitic stainless steels, both cold worked and solution annealed, hold the world's record in the quality index which is the product of strength times toughness. It appears extremely difficult, if not impossible to reach  $8 \times 10^5 \text{ MPa}^2\sqrt{\text{m}}$  by the year 2000.

One reason why it might be difficult to go far beyond the present limits is the possibility of cleavage cracking which we have observed already, albeit at cryogenic temperatures. Nevertheless, by proper cold working schedules we hope to exceed the present limits which are indicated by the shaded area in Fig. 3. A survey of all metallic and nonmetallic materials has shown that this shaded area in Fig. 3 defines the high nitrogen austenitic stainless steels as the group of materials which outperforms every other material in terms of strength times toughness today. Note however, that Fig. 3 applies only at ambient temperatures. At cryogenic temperatures the situation may be entirely different.

## Stress Corrosion Cracking

There is no ultrahigh strength steel (with yield strength of 1500 MPa and more) which is not susceptible to stress corrosion cracking in water at ambient temperature - save cold worked high nitrogen austenitic stainless steels. This is illustrated in Fig. 4. Note that the widely used steel 4340 (41SiNiCrMoV 76) cracks at a rate of about  $10^{-5} \text{ m/s}$  while the cold worked high nitrogen austenitic stainless steel P900 cracks at a rate of less than  $2 \times 10^{-11} \text{ m/s}$ . In fact, it does not exhibit any observable stress corrosion crack growth, but  $2 \times 10^{-11} \text{ m/s}$  is our limit of resolution.

It is this resistance to stress corrosion cracking which has made generator rotor retaining rings a highly successful product when manufactured of cold worked high nitrogen austenitic steels. However, this application demonstrates also that a combination of the outstanding properties high nitrogen steels can give may be necessary in a single product: here it is nonmagnetic behavior, strength, toughness and stress corrosion cracking resistance.

### Magnetic Properties

Austenitic steels are often used because they are not ferromagnetic. However, as these steels are cold worked to obtain higher yield strength levels, they may develop transformation martensite. The corresponding increase in magnetic permeability is shown in Fig. 5. Note that steels with increasing amounts of alloying elements which stabilize the face centric cubic crystal lattice can take more and more cold work before transformation martensite and the corresponding ferromagnetism are observed. Nitrogen is the most potent austenite stabilizer and therefore, high nitrogen austenitic steels do not show transformation martensite during cold work - at least not the steel X5CrMnN18 18 with 0.6 weight-percent nitrogen, as shown in Fig. 5. Since certain applications depend on the absence of ferromagnetism, high nitrogen austenitic steels may be a good selection.

The observation that high nitrogen austenitic steels do not develop transformation martensite may help to understand their resistance to stress corrosion cracking in water. This is because untempered martensite is known to be particularly susceptible to stress corrosion cracking.

### Creep Resistant Ferritic High Nitrogen Steels

Carbonitrides which precipitate from martensite in 9 to 12 percent chromium steels can be more homogeneously distributed and more stable than the usual carbides used in conventional 9 to 12 percent chromium steels of the type X20CrMoV12 1. The finer distribution of the carbides is due to an easier mechanism of nucleation

which results from the crystal structure of the nuclei. It is also well known that nitrides and carbonitrides are thermodynamically more stable than carbides. One of the results of the finer, more uniform and more stable distribution of particles is shown in Fig. 6. Such steels are more resistant to creep than conventional 12% chromium steels, thus offering the possibility to raise the inlet temperature of steam in steam turbines by 50°.

The fine distribution of carbonitrides also results in better combinations of strength and toughness in a high temperature range which is not yet creep critical. Thus there is reasonable hope to use high nitrogen 12% chromium steels for compressor and gas turbine discs in the temperature range up to 500°C.

#### Wear and Abrasion Resistance

Wear and abrasion resistance is not easily understood or predicted from a fundamental point of view. However, it is generally agreed that wear and abrasion resistance depend on a combination of strength, toughness and corrosion resistance. All these properties, however, can be developed in high nitrogen austenitic steels, as indicated above. Therefore, exceptional wear resistance under certain conditions may be expected and is, indeed, observed in a number of new trial applications. These and further properties and applications will be more fully reported in other contributions to HNS90 from the author's ETH Institute in Zurich.

#### Acknowledgments

The author wishes to thank his coworkers at the Institute of Metallurgy, ETH Zurich, for their contributions to the understanding and improving of the properties of high nitrogen steels.

Close cooperation with Vereinigte Schmiedewerke, Essen is highly appreciated.

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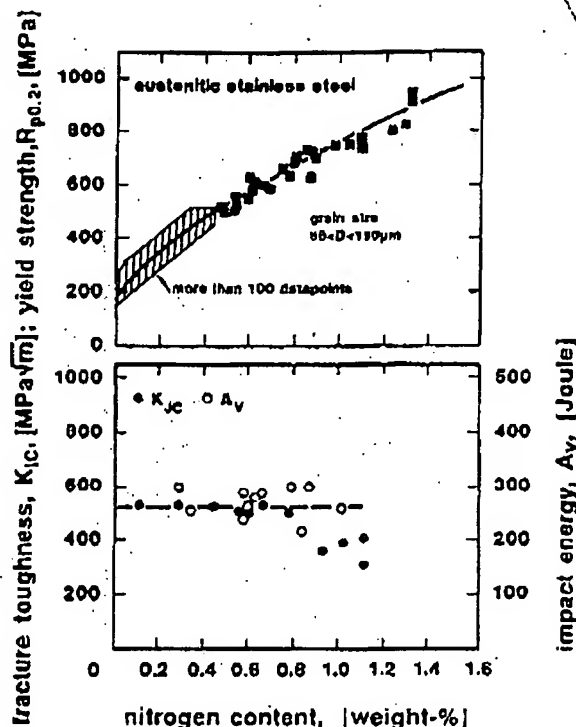


Fig. 1 Effect of nitrogen in solid solution on strength and toughness of solution annealed austenitic stainless steels measured at ambient temperature.

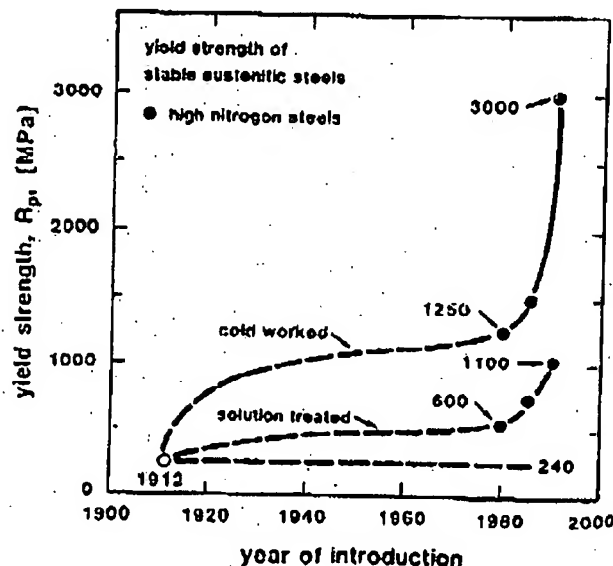


Fig. 2 During the last few years, the successful development of high strength stable austenitic stainless steels has greatly accelerated.

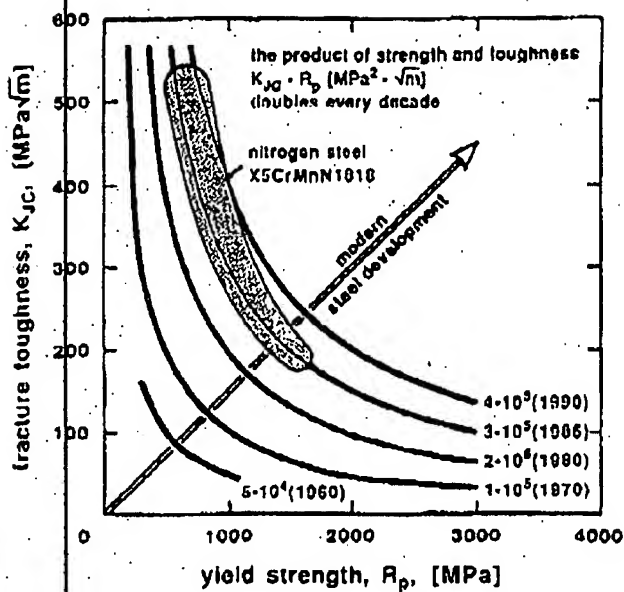


Fig. 3 Of all steels, and indeed of all materials available today, high nitrogen austenitic steels have the highest combination of strength and toughness.

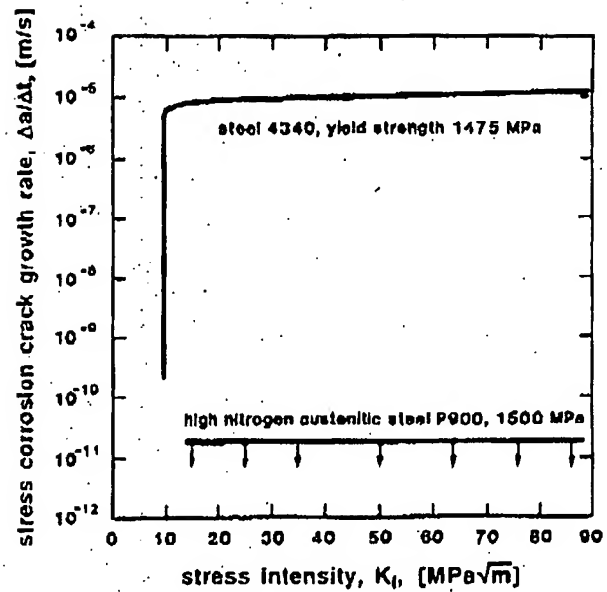


Fig. 4 High nitrogen, cold worked austenitic stainless steels are the only ultra-high-strength steels available today, which are not susceptible to stress corrosion cracking in water at ambient temperature.

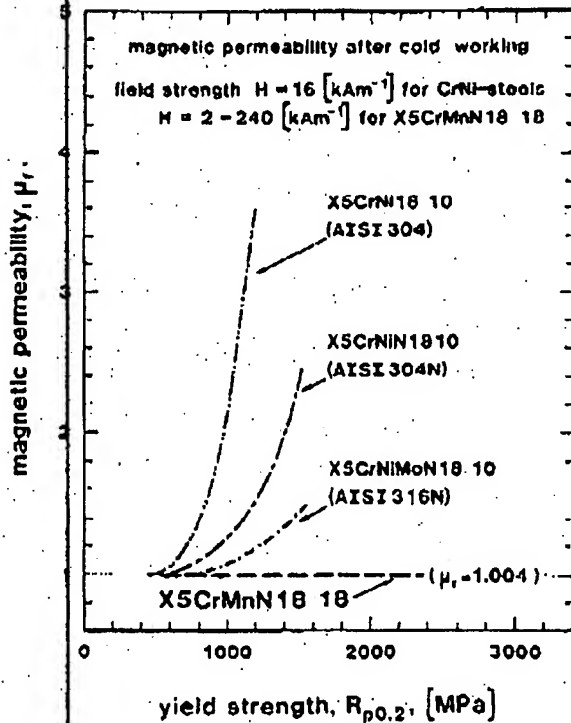


Fig. 5 High nitrogen nonmagnetic austenitic stainless steels can be cold worked to very high strength levels and still do not form ferromagnetic transformation martensite.

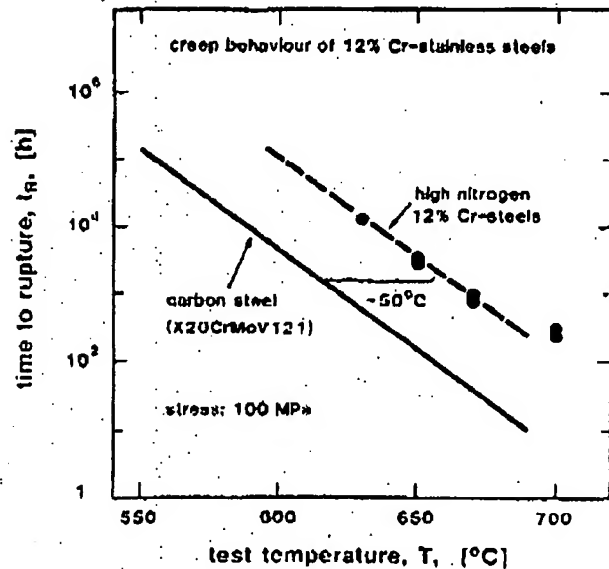


Fig. 6 Nitrogen in 12% chromium steels results in the precipitation of stable carbonitrides. Such steels are more resistant to creep than conventional 12% chromium steels, thus offering the possibility to raise the inlet temperature of steam turbines by 50°C.